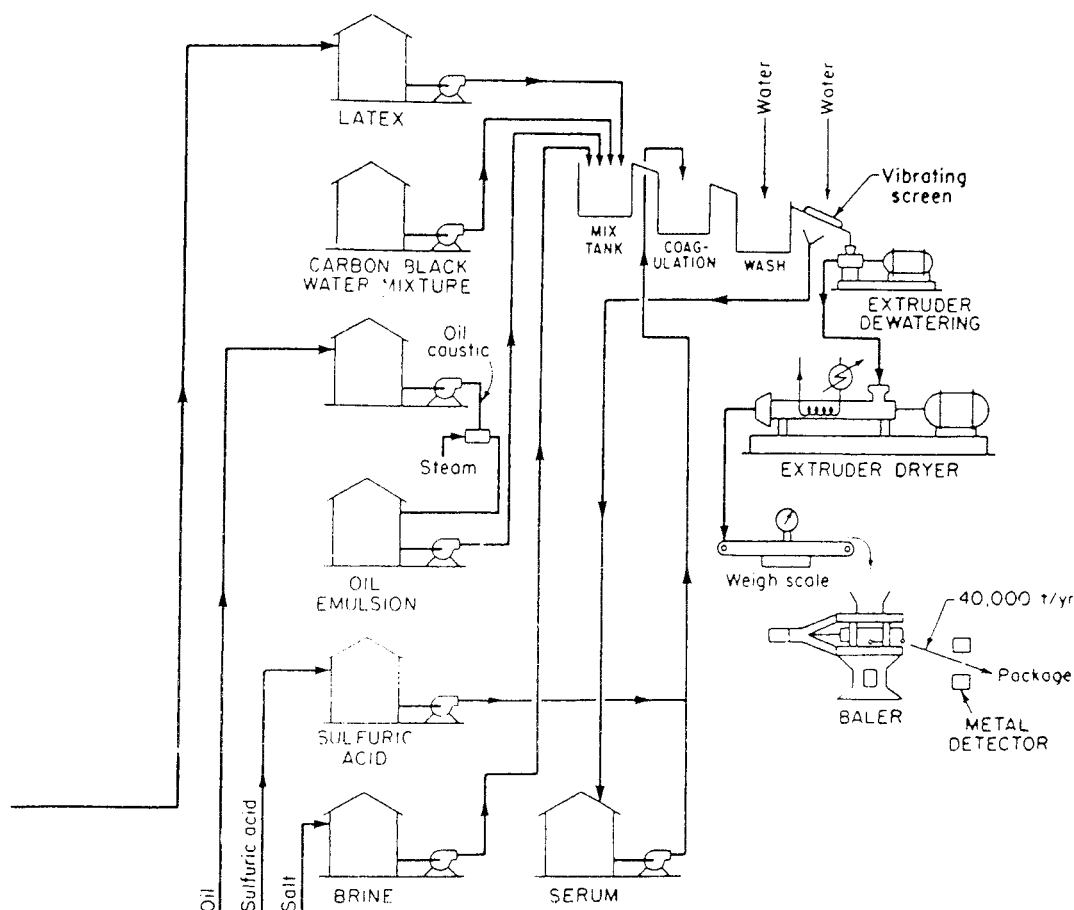


nant quality considerations. See Stereospecific Copolymers. The ability to control molecular weight has led to the development of *oil-extended rubbers* (Fig. 36.4), which have had far-reaching effects on the industry. In late 1950, the General Tire & Rubber Co. applied for a patent and disclosed its process for the addition of petroleum oils to high-molecular-weight rubber. Not only does the oil render the extremely tough, high-molecular-weight rubber processible, but it allows much of the quality inherent in the tougher material to be retained and actually results in improvements in quality. Amounts of oil up to 50 parts per 100 parts rubber have become commonplace, and approximately 70 percent of the SBR produced in the United States is oil-extended, finding its principal use in tire-tread rubber. First successfully applied to SBR, the process has assumed great importance as ways to add oils to the newer stereoregular polymers have been discovered.

**MONOMER RECOVERY.** The rubber quality and rate of reaction both fall off as polymerization proceeds, and it is customary to stop the reaction short of complete conversion to rubber. Recovery of the unreacted monomers and purification is an essential step in economical synthetic-rubber production (Fig. 36.4). Methods of recovery by steam stripping from aqueous latices or by distillation from solvent systems are employed. In some cases, recovery of the monomer can be accomplished during the drying step in a devolatilizing extruder dryer as pictured in Fig. 36.6. Water or solvent is removed by a combination of mechanical squeezing and by passage through a vacuum section. The space, maintenance, and labor requirements of such dryers are sufficiently less than for the conventional multipass apron dryer, so that this unit has been installed in several new rubber plants.



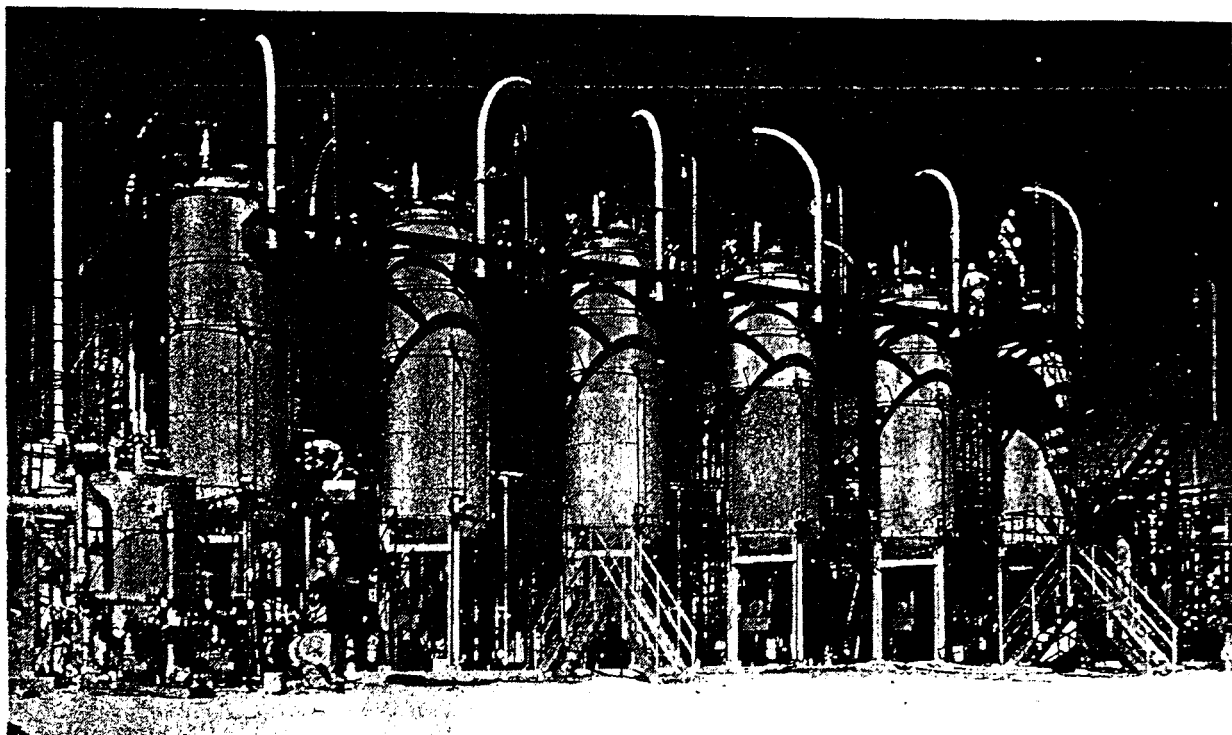


Fig. 36.5. Synthetic rubber reactors operated in series for a continuous reaction to produce SBR (General Tire and Rubber Co.)

**COAGULATION AND DRYING.** The finishing process usually consists of precipitating the rubber from the latex emulsion or from the solvent solution in crumb form; it is then dried and compressed into a bale (Fig. 36.6). Ordinary latices may be easily coagulated by the addition of sodium chloride and dilute sulfuric acid, alum, or virtually any combination of electrolyte and dilute acid. The rubbers which result from solution polymerization can be precipitated into crumb form by adding the solution to a tank of hot water under violent agitation, with or without the addition of wetting agents, to control crumb size and prevent reagglomeration. The coagulated crumb is separated from the serum and washed on vibrating screens or rotating filters and dried at appropriate temperatures. Rubber is a difficult material to dry, and care must be taken not to overheat it or otherwise cause its deterioration. Drying times in conventional hot-air apron dryers may be as long as several hours.

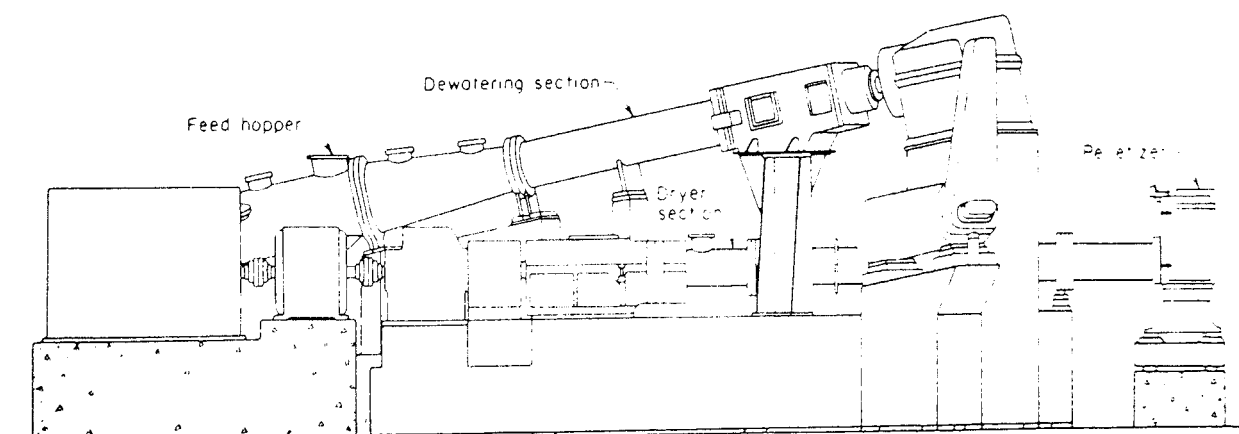


Fig. 36.6. Dual worm rubber dryer or dewaterer. This accepts a slurry feed of 50% or more solids containing 1 to 2% hydrocarbons and devolatilizes and dries to less than 0.3% volatiles. Throughput rates are up to 2300 kg/h with continuous feed, using 485 kJ and 315 MJ/h jacket heating. Typical elastomers handled by this equipment are butyl rubber, *cis*-polybutadiene, and *cis*-polyisoprene. (Welding Engineers)

**PACKAGING.** Synthetic-rubber packaging is important, since problems involving adherence to the package and contamination resulting from inadequate protection are sometimes difficult to cope with because of the tendency of some of the rubber to flow and fail to retain its shape. Most rubber is now wrapped in polyethylene film as a 34-kg bale of reasonably standard dimensions. In most cases, it is possible to throw bale and polyethylene wrapping into the rubber mill or internal mixer, since the polyethylene melts at a temperature lower than the usual rubber-processing temperatures.<sup>8</sup>

**BUTADIENE-STYRENE COPOLYMERS.**<sup>9</sup> The copolymers of styrene and butadiene that contain over 50% butadiene are known as SBR. The usual monomer ratio is 70 to 75 parts of butadiene to 30 to 25 parts of styrene. As the styrene content is increased above 50%, the product becomes increasingly plastic and is used in latex paint. A typical recipe for SBR is given in Table 36.6. The polymerization is carried out in an emulsion at about 5°C and requires 8 to 12 h. A series of reactors, such as those shown in Fig. 36.5, are often used. The heat of polymerization is approximately 1280 kJ per kilogram of rubber produced and is removed by internal ammonia coils. The molecular weight of the polymer is regulated by the use of a modifier, such as a tertiary C<sub>12</sub> mercaptan, which regulates chain growth. The reaction is terminated at 60 to 75 percent of completion because higher conversion gives polymers with inferior properties that are due to cross-linking and branching. Sodium nitrite and sodium dimethyldithiocarbamate are added to terminate the reaction. The unreacted butadiene is flashed off, and the styrene is recovered by steam distillation.

The emulsion, in effect a latex,<sup>10</sup> is accumulated in holding tanks and blended to the proper specifications for the grade of rubber required. It is coagulated and extensively washed and dewatered prior to the drying operation. Much of the SBR is extended with oil before it is vulcanized. The softening effects of the oil are counterbalanced by the addition of carbon black. Much of the SBR sold is in the form of master batches, in which the oil and carbon have already been added.

Emulsion polymerization produces a random distribution of the polymer units. A typical SBR produced by emulsion polymerization contains 23% styrene units, and the butadiene units (77% of the total) have the configuration of 65% *trans*-1,4, 18% *cis*-1,4, and 17% vinyl-1,2.

Styrene-butadiene copolymers may also be produced by solution polymerization. Solution

<sup>8</sup>Rubber Handling: Crumb to Bale, *Hydrocarbon Process.* 53 (3) 79 (1974).

<sup>9</sup>ECT, 3d ed., vol. 8, 1979, p. 608; Saltman, *op.cit.*

<sup>10</sup>Suspension of rubber particles 40 to 200 nm in size

**Table 36.6** Typical Recipe for Cold Emulsion SBR

	Parts by Weight	Function
Butadiene	72	Monomer
Styrene	28	Monomer
<i>d</i> -Isopropyl benzene hydroperoxide	0.08	Catalyst
Ferrous sulfate	0.14	Activator
tert-Dodecyl mercaptan	0.2	Modifier
Potassium pyrophosphate	0.18	Buffer
Rosin acid soap	4.0	Emulsifier
Water	180	

SOURCE: Allen, *Natural Rubber and the Synthetics*, Wiley, New York, 1972.

polymerization allows the operator to have some control over the stereostructure of the resulting polymer and thus, over the physical properties. A typical solution SB polymer contains 35 to 40% *cis*-1,4, 50 to 55% percent *trans*-1,4, and 10% vinyl-1,2-butadiene units. The styrene units are randomly distributed along the chain. This polymer has better abrasion and fatigue resistance, higher resilience, and lower heat build-up than emulsion polymerized SBR.

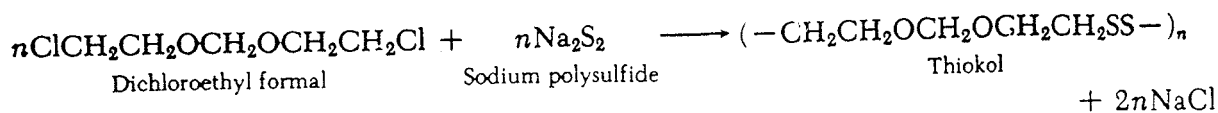
Block polymers of styrene and butadiene may also be produced by special polymerization conditions (Chap. 34). These polymers are thermoplastic and do not require vulcanization to be useful.

SBR rubber does not crystallize when stretched, as natural rubber does, and thus is very weak unless reinforced with carbon black or other materials. It is, even then, less strong than natural rubber. Its vulcanization properties are good and the ageing characteristics are satisfactory. Over 70 percent of the SBR produced is used for tire and tread rubber, 15 percent for mechanical goods, and about 10 percent is sold as latex.

**NITRILE RUBBERS (NBR).** Copolymers of butadiene and acrylonitrile are made similarly to SBR by emulsion polymerization. The acrylonitrile content of the copolymer may be varied from 20 to 50% depending upon the properties desired. Resistance to hydrocarbons, solvents, abrasion, and gas permeation increases with increasing nitrile content. Decreasing the amount of nitrile present increases the low-temperature properties and resilience. NBRs are resistant to oils, solvents, water, salts, aliphatic compounds, soaps, and most foods. They are serviceable for continuous use up to 120°C in air and to 150°C immersed in oil.

**NEOPRENE.** Polychloroprene was developed by DuPont and sold commercially in 1932, first under the name DuPrene, but later as Neoprene. It is prepared by emulsion polymerization of purified chloroprene at about 38°C in the presence of sulfur. It is resistant to oxidation, oil, and heat, is flame resistant, and finds specialty uses, especially in automotive parts, adhesives, sealants, and coatings. It is more expensive than natural rubber and thus is only used where its special properties are needed.

**THIOKOL.** Thiokol, a polysulfide type of rubber, was first developed in this country in the early 1920s and was the first commercial synthetic rubber produced in the United States. Thiokols are prepared by the condensation polymerization of an alkaline polysulfide with a suitable organic dihalide.

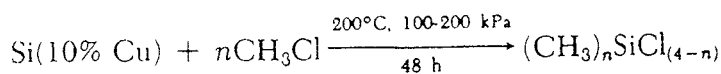


Various sodium polysulfides may be reacted with organic dihalides to give specialty rubbers of somewhat different properties, and are particularly useful for linings for petroleum tanks, for building and caulking putties, cements, and sealants, and lately for rocket-fuel binders, ablative coatings, and other items requiring ease of application and good weathering resistance.

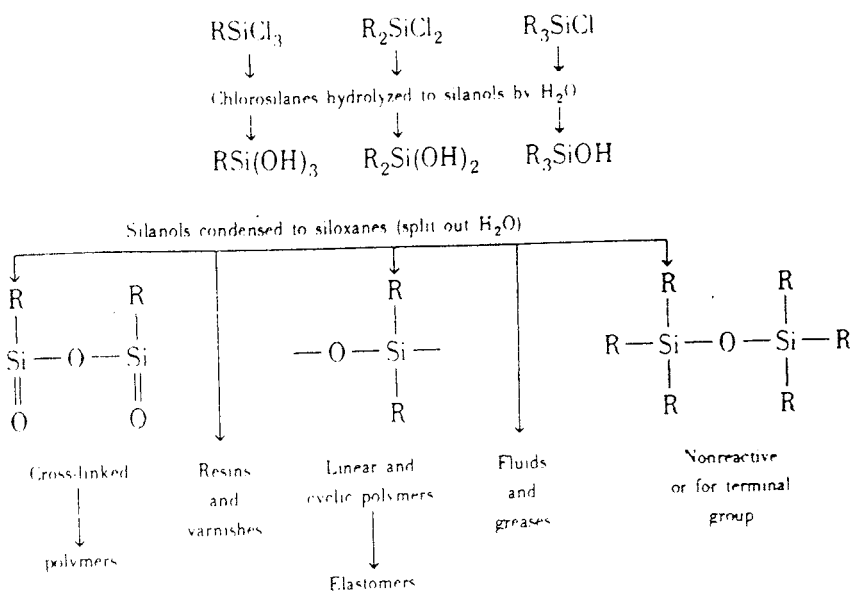
**SILICONE RUBBERS.** Silicone rubbers are mixed inorganic-organic polymers produced by the polymerization of various silanes and siloxanes. Although expensive, their outstanding resistance to heat makes them uniquely useful for high-temperature applications. The chain is based on alternate atoms of silicon and oxygen, with no carbon. Silicones and their derivatives are remarkable in the variety and unusualness of their properties, such as solubility in

organic solvents, insolubility in water and alcohols, heat stability ( $-62$  to  $200^{\circ}\text{C}$ ), chemical inertness, high dielectric properties, relatively low flammability, low viscosity at high resin content, low viscosity change with temperature, and nontoxicity. Because of these properties, silicones are useful in fluids for hydraulics and heat transfer, lubricants and greases, sealing compounds for electrical applications, resins for lamination and for high-temperature-resistant varnishes and enamels, silicone rubber, water repellents, and waxes and polishes. The largest consumption of silicone rubbers is by the aerospace industry which uses them for de-icing equipment, gaskets, ablation shields, and similar temperature-demanding applications.

Silicones<sup>11</sup> are made either by the Grignard reaction, or more economically, by alkylating with an organic halide, usually  $\text{CH}_3\text{Cl}$  (or  $\text{C}_6\text{H}_5\text{Cl}$  or mixtures thereof), and a silicon-copper alloy, according to the following reaction:



The principal products are the chlorosilanes:  $(\text{CH}_3)_2\text{SiCl}_2$ ,  $(\text{CH}_3)_3\text{SiCl}$ ,  $\text{CH}_3\text{SiCl}_3$ . The chain length of the polymers is varied by the percentage of  $\text{R}_3\text{SiCl}$ , which provides the end groups. Lower polymers are oils, higher polymers are solids. The silicon or copper may absorb any excess chlorine. Further reactions to silanols, siloxanes, and polymers may be expressed:



The production of silicone products for elastomers in 1978 was  $27 \times 10^6$  kg worth about \$210 million.

**BUTYL RUBBER.** The copolymer of isobutylene with about 2% isoprene is known as butyl rubber. The isoprene imparts sufficient unsaturation to the molecule to permit curing or vulcanization. The polymerization is carried out in a slurry of the monomers in methyl chloride using an aluminum chloride catalyst at  $-100$  to  $-90^{\circ}\text{C}$ . The reaction is very fast and produces 2000+ monomer linkages.<sup>12</sup> The rubber is precipitated by adding water and separates

<sup>11</sup>Rochow, *An Introduction to the Chemistry of the Silicones*, 2d ed., Wiley, New York, 1936; *General Electric Materials Technology*, spring 1980; Schiefer and Pope, Use of Silicones in Process Plants, *Chem. Eng.* 89 (3) 123 (1982).

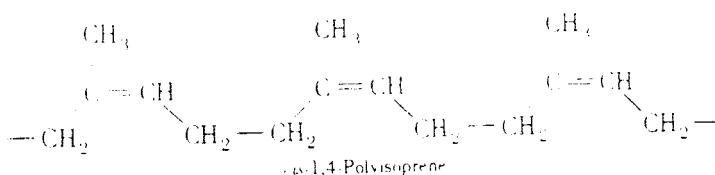
<sup>12</sup>ECT, 3d ed., vol. 8, 1979, p. 470.

as a crumb. Butyl rubber has extremely low permeability to gases and thus its major use is in inner tubes and in linings for tubeless tires. Butyl rubber is also inert to oxidation and is useful for weatherstripping. A variant, halogenated butyl rubber, has even better resistance to ageing, is more compatible with other rubbers, and is used in tubeless tires.

**URETHANE RUBBER.** The reaction products of certain organic diisocyanates and polyglycols are rubbery products known as polyurethanes.<sup>13</sup> These compounds are specialty rubbers with outstanding properties as they possess high abrasion resistance and are useful at high temperatures and with high concentrations of solvents and oxygen or ozone. A major use for this type of rubber is in the production of flexible foam and elastic fibers, which result when a diisocyanate is mixed with a polyester containing both free hydroxyl and carboxyl groups. The reaction is extremely rapid, with the evolution of gas which serves to expand the mass yielding foams, either hard or soft, depending on the reactants and the conditions employed. These materials have found increasing use in upholstery, mattresses, insulation, vibration damping, and other fields of application formerly restricted to foam rubber. The tensile strength and abrasion resistance of polyurethanes are extraordinary in comparison with those of hydrocarbon elastomers. Both rigid and flexible foams have encountered difficulties in some applications because of flammability. The appearance of spandex (Chap. 35) polyurethane elastic thread has revolutionized the support-garment field because of the high holding power of fine-denier thread.

**HYPALON.** A rubber called Hypalon results from the free-radical catalyzed reaction of chlorine and SO<sub>2</sub> with polyethylene, transforming the thermoplastic polyethylene into a vulcanizable elastomer. Hypalon is extremely resistant to ozone attack, weathering, and heat and has excellent chemical resistance.

**STEREOSPECIFIC RUBBER- POLYISOPRENE AND POLYBUTADIENE.** The discovery that catalysts of the Ziegler-Natta (alkyl lithium) type would catalyze polymerization of isoprene or butadiene to produce mainly the *cis* structure made it possible to nearly duplicate natural rubber synthetically. Polyisoprene (IR) is



and is essentially identical with natural rubber and has the advantages of being of better color, more uniform in quality, lower odor, faster processing breakdown and mixing, better extrusion and calendaring, excellent mold flow, and a controlled molecular weight. In contrast, natural rubber has higher tear strength, tack, and tensile strength. IR is produced commercially and is used along with, or substituted for, natural rubber (Fig. 36.7).

The lower cost and availability of butadiene, relative to isoprene, have caused polybutadiene to be produced in much greater quantities than polyisoprene (Table 36.5). It is the third most used rubber after SBR and NR. Stereoregular polybutadiene (BR) can be produced in

<sup>13</sup>Frisch and Reegan, *Advances in Urethane Science and Technology*, Technomic, Westport, Conn., vols. 1-7, 1971-1979; *Urethane Chemistry and Applications*, ACS, Columbus, Ohio, 1981.

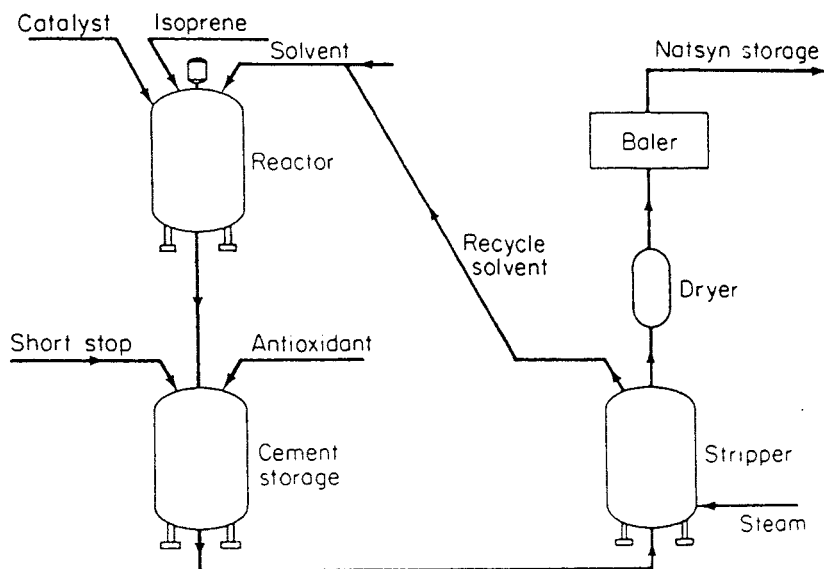


Fig. 36.7. Natsyn process for synthetic natural rubber production (synthetic polyisoprene) (Goodyear Tire and Rubber Co.)

modified SBR plants. The catalyst used determines the configuration of the polymer.<sup>14</sup> If a Ziegler-type catalyst (organic aluminum compound plus a titanium, cobalt, or nickel compound) is used, polymers of up to 90% *cis* form can be produced. On the other hand, anionic catalysts, such as butyl lithium, produce polymers containing about equal quantities of *cis* and *trans* forms, while vanadium chloride or rhenium and nickel complexes yield almost pure *trans* form. The other type of polymer obtained from 1,4-butadiene is the vinyl- or 1,2-polybutadiene. This can be produced in good yields using a halogen-free vanadium compound with an aluminum alkyl as a cocatalyst.

High *cis*-1,4-polybutadienes are soft, easily solubilized, and have low hysteresis and good abrasion resistance. High *trans*-1,4-polymers are rigid, crystalline, and have poor solubility characteristics. These can be used to replace gutta-percha for golf ball covers. The usual polybutadiene rubbers produced are alkyl lithium catalyzed and contain medium amounts of the *cis* isomer. Polybutadiene is used to extend and partially replace both NR and SBR in tires. The usual tire contains 25% polybutadiene, and this use accounts for 85 percent of the butadiene produced.

**ETHYLENE-PROPYLENE POLYMERS AND TERPOLYMERS.**<sup>15</sup> Copolymers of ethylene and propylene (EPM), made by solution polymerization using a Ziegler-type catalyst, are elastomers but do not contain any double bonds. Thus, they cannot be vulcanized but neither are they attacked by oxygen and ozone. The reactivities of ethylene and propylene are quite different, and thus the monomer composition differs from that of the copolymer formed. This offers difficulties in preparing a uniform polymer and requires that the monomer composition be kept constant during the course of the polymerization. EPR may be vulcanized by heating with a peroxide which cross-links the chains by joining carbon atoms directly to each other, instead of through a sulfur linkage as in the usual process. These rubbers may be used without vulcanization for many purposes.

<sup>14</sup>ECT, 3d ed., vol. 8, 1979, p. 546.

<sup>15</sup>Walker (ed.), *Handbook of Thermoplastic Elastomers*, Van Nostrand Reinhold, New York, 1979; Saltman, op. cit.; Allen, op. cit.

To promote easier vulcanization, terpolymers of ethylene-propylene and a diene (EPDM) have been prepared. The diene is used only in very small amounts and should contain one double bond that is capable of polymerizing with ethylene and propylene and one that can be used for vulcanization. It is also desirable that the second double bond not be in the main chain of the finished polymer. Conjugated double-bond compounds are not suitable. Compounds such as 1,4-hexadiene and dicyclopentadiene are commonly used.

EPDM polymers are exceptionally resistant to heat, oxygen, and ozone, and are widely used as roofing materials where they are replacing hot asphalt. Other uses are in wire and cable insulation where they are competing with neoprene.<sup>16</sup>

## RUBBER COMPOUNDING

Pure rubber (natural or synthetic) is usually not suitable for use. The desirable properties of plasticity, elasticity, toughness, hardness or softness, abrasion resistance, impermeability, and the myriad combinations possible are achieved by the art of the rubber compounder.<sup>17</sup> A typical rubber compound is shown in Table 36.7. Rubber-processing chemicals production in 1980 was 132,000 t. Sales were 88,000 t and were valued at \$296 million.<sup>18</sup>

These chemicals are divided into groups according to their uses (Table 36.8).

The *vulcanizing agents* are usually sulfur compounds which react with the polymer to produce a cross-linked material in which the linkages are  $-C-S_x-C-$ . The cross links may be mono-, di-, or polysulfidic. The type of linkage is determined by the concentrations of sulfur, accelerators, and retarders, and temperature. Most of the conditions to produce a given product are empirical, but some advances in knowledge are beginning to allow a scientific basis for vulcanizing conditions.

The *accelerators* reduce the time required for the vulcanization of rubber from several hours to a few minutes. In addition, less sulfur is needed and a more uniform product is obtained. The mechanism of accelerator action is not well understood, in spite of much research, but presumably involves the formation of an activated form of sulfur, which forms a "sulfur bridge" at reactive sites within the rubber molecule, linking the large molecules into

<sup>16</sup>EPDM Finds a Home as a Roofing Material, *Chem. Week* 128 (17) 13 (1981); Uniroyal Copolymer Challenges Neoprene, *Chem. Eng. News* 60 (35) 5 (1982).

<sup>17</sup>*Additives for Rubber and Plastic*, Chemical Marketing Research Association, 1977; Coran, The Art of Sulfur Vulcanization, *CHEMTECH* 13 (2) 106 (1983).

<sup>18</sup>*Synthetic Organic Chemicals, 1980, U.S. Production and Sales*, U.S. International Trade Commission, 1981.

**Table 36.7** Typical Rubber Compound

Ingredient	Parts	Ingredient	Parts
Rubber	100.0	Loading or tilling pigment	50.0
Sulfur	2.0	Reclaim, softeners, extenders, colors, blowing agents, antioxidants, antiozonants, odorants, etc.	As required
Zinc oxide	5.0		
Stearic acid	3.0		
Accelerator	1.5		



**Table 36.8** Rubber-Processing Chemicals

Type of Agent	Chemical Compounds
Vulcanizing or curing	Sulfur, sulfur monochloride, selenium, tellurium, thiuram disulfide, polysulfide polymers, <i>p</i> -quinone dioxime
Accelerators	2-Mercaptobenzothiazole, benzothiazolyl disulfide, zinc diethyldithiocarbamate, tetramethyl mono- and disulfides, 1,3-diphenylguanidine
Accelerator activators	Zinc and magnesium oxides, stearic acid litharge, amines, amine soaps
Retarders	Salicylic and benzoic acids, phthalic anhydride
Antioxidants	<i>N</i> -Phenyl-2-naphthylamine, alkylated diphenylamine, acetone-diphenylamine condensate
Antiozonates	Derivatives of <i>p</i> -phenylene diamine
Fillers	Carbon black, clays, silica, zinc oxide, calcium carbonate
Softeners and extenders	Petroleum oils, pine tars and resins, coal-tar fractions
Blowing	Sodium or ammonium bicarbonate, diazoaminobenzene, dinitrosopentamethylenetetramine, fluorocarbons, azodicarbonamide nitrosoterephthalimide
Chemical plasticizers	2-Naphthalenethiol, bis( <i>o</i> -benzaminophenyl)disulfide, mixed xylene thiols
Peptizers	Aromatic mercaptans (thiophenols)

a tight network structure. Most accelerators contain nitrogen and sulfur. Two-thirds of all the accelerators made consist of mercaptobenzothiazole (MBT) and its derivatives. The commercial process for the manufacture of MBT comprises reacting aniline, carbon bisulfide, and sulfur at a temperature of about 250°C and a pressure of at least 3.1 MPa. The crude product is dissolved in caustic, insoluble tars are removed, and the resulting solution is used for the manufacture of various derived accelerators, including refined MBT, benzothiazyl disulfide (MBTS), the zinc salt of MBT, and *N*-cyclohexylbenzothiazole sulfanamide.

*Age resisters, or antioxidants*, protect rubber goods from attack by oxygen and ozone in the atmosphere. They are classified as antioxidants, antiozonants, or antiflex-cracking agents. They function by combining with, and thus interrupting, free-radical chain reactions and thus prevent further chain degradation. Commercial age resisters are generally either of the amine type or the phenolic type. Amines are strong protective agents and are widely used in tires and other dark-colored goods where discoloring or staining is not a problem. Examples of amine age resisters are alkylated diphenylamines, alkylated and arylated *p*-phenylenediamines, and complex reaction products of aromatic amines with aldehydes or ketones. In the case of light-colored goods, alkylated phenols and their derivatives are used to give moderate antioxidant protection with minimum discoloration.

Catalytic plasticizers, or *peptizers*, serve to reduce the viscosity of rubber to permit easier processing. When milled into the rubber, they cause chain scission, with a consequent lowering of the molecular weight. Peptizers are useful both in reclaiming vulcanized rubber and in softening high-molecular-weight crudes.

Large amounts of *inert filling materials* may be added to rubber. Some merely serve to harden or to dilute the mix. Others exert a profound influence called reinforcement, which is chemicophysical in nature. Clays, calcium carbonate, crushed coal, barytes—almost any finely divided solid—can be added to rubber, usually with a reduction in all tensile properties but with a desirable cost reduction, along with imparted hardness, retention of shape, color,

and other desirable properties. However, some finely divided amorphous materials, notably *carbon black* and *silica*, unexpectedly greatly increase the strength, resilience, abrasion resistance, and other desirable properties and are properly known as reinforcing agents.

*Processibility* is improved by the use of reclaimed rubber, waxes, oils, factices (vulcanized vegetable oils), and mineral rubbers (asphalts, pitches, and vulcanized unsaturated hydrocarbons) or by chemical attack on the molecule, as well as by work breakdown, heat, and mastication.

*Sponge structure* is obtained by adding sodium bicarbonate, ammonium carbonate and bicarbonate, urea, or organic gas-generating chemicals. *Hard rubber* may be made by greatly increasing the sulfur content and by the use of large amounts of filler.

## RUBBER FABRICATION

As a plastic material, rubber may be spread, cemented, calendered, molded, extruded, caulked, puttied, or wrapped into virtually any shape; coated on cloth, plastic, or metal, and sandwiched or forced into cracks. Rubber is an extremely tough material. Heavy machinery is required, some of which is shown in the flowchart of Fig. 36.8 and in Figs. 36.9 and 36.10. The considerable heat generated during the mixing, mastication, grinding, and extruding must be dissipated and controlled. Some typical rubber-goods manufacture is briefly described.

**CALENDERING, OR COATING.** One of the earliest uses for rubber was for coating fabric to make it waterproof. Solutions or cements of rubber in solvents are easily spread on fabrics but, unless the ingredients necessary for cure and property control are included, the results may be quite unsatisfactory. Rubber compounds are applied to fabric by calendering, i.e., rolling the rubber compound into the fabric on multiroll calender machines. Tire cord is a special case in which cotton, rayon, nylon, or polyester cords are arranged in parallel and bound together by rubber on a calender.

**MOLDING.** Doughlike rubber compounds may be molded into virtually any shape, which is retained by curing the compound in the mold. A tennis ball is a good example. A very high grade and resilient rubber compound is molded in "muffin tins" shaped as halves of the ball. These are cemented together (with a pill of a gas-releasing chemical enclosed) and vulcanized to form the core of a ball, to which the fabric cover and proper nap fiber are cemented. It is a complicated structure for very rugged service.

**EXTRUDING.** Weatherstrip, hose, inner tubes, tire treads, gaskets, channels, and many other rubber articles are fashioned by extrusion of the plastic compound, which may be cured during this operation or later. The automobile tire serves as an example. Transportation is the major end use of rubber, and the tire its supreme product. Tire manufacture is depicted in Figs. 36.8 to 36.10. These illustrations show the many steps involved and make clear how the tire is shaped from wire, cord, fabric, and rubber into the doughnut shape which hugs the vehicle rim, retains air for months or years, resists the heat built up by service and the attack of air, ozone, oils, and chemicals, and provides tens of thousands of miles of travel over roads and highways of all types and all of a highly abrasive nature.

The tire is *built up as a cylinder* on a collapsible, round rotating drum. Layers of cords embedded in a proper compound are applied, one layer tying the beads together in one direc-



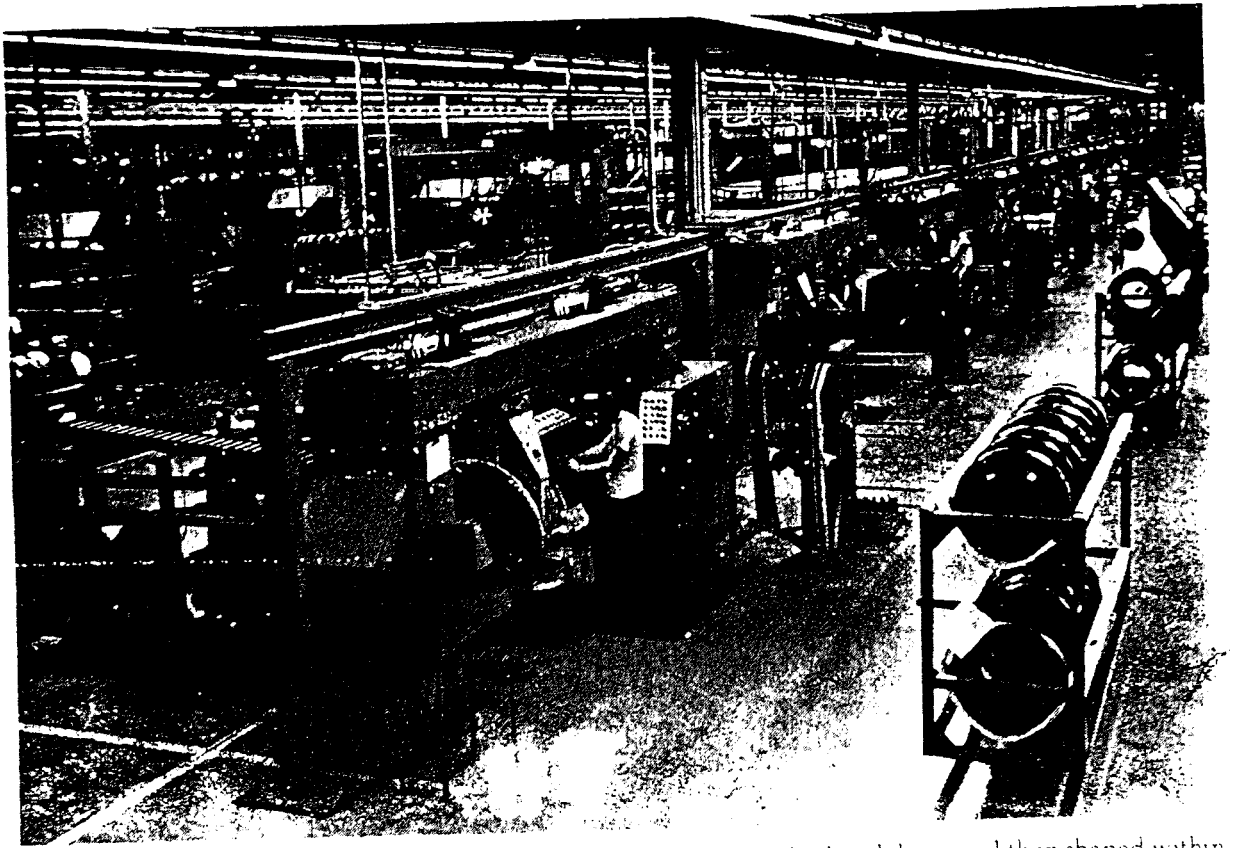


Fig. 36.9. Radial-tire building machine. The carcass is built on a cylindrical drum and then shaped within the tread and bell. (*General Tire and Rubber Co.*)

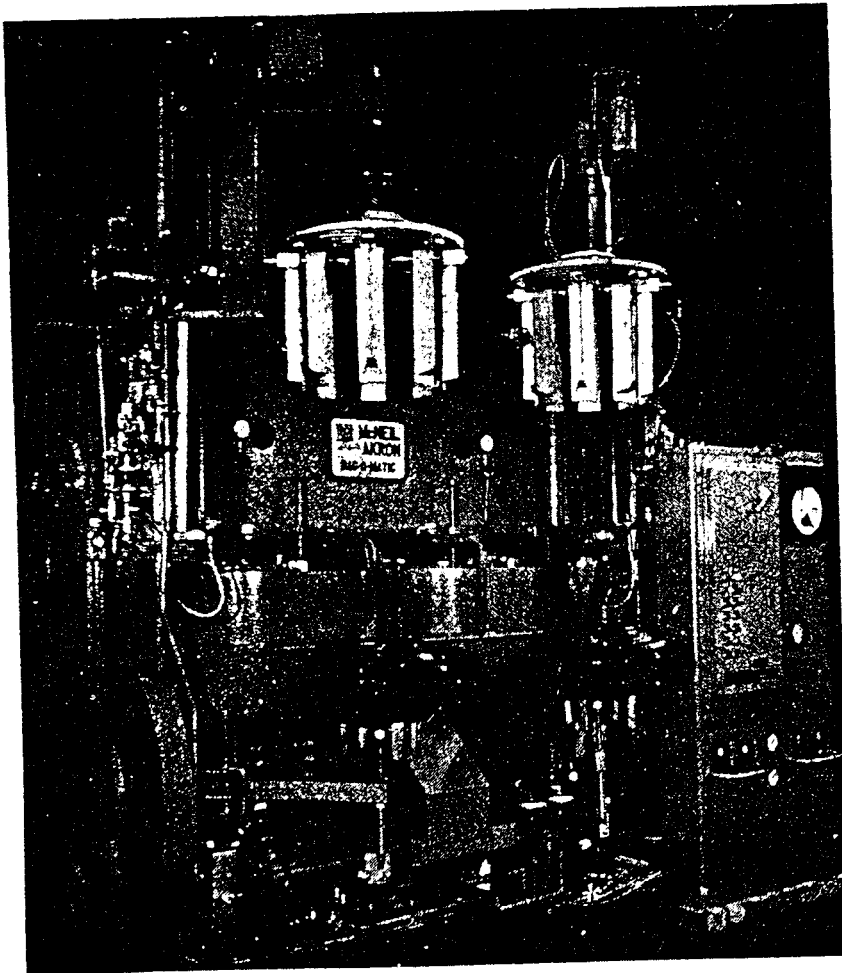


Fig. 36.10. Twin Bag-o-matic tire curing press with segmented-mold operating cylinders. Radial tires are shaped to approximately their final appearance and vulcanized in molds such as these.

tion and another layer in another direction. The beads—wire cables embedded in a tough, hard rubber—are “stitched” to the tire by folding the end of the cord fabric over. Last, the tread formed by extrusion is laid on, and the ends lapped together. The tire-building drum is collapsed, and the cylindrical tire removed and placed in a press. Here an inflatable rubber bag, usually made from butyl rubber and on a movable stem, is blown up inside the tire; the press mold is simultaneously closed, and the tire becomes a doughnut. Heat is applied through the mold and by steam inside the bag. Excess rubber escapes through weep holes and, after a timed cure at preselected temperature, the tire is formed. Present-day tires may be tubeless, with the air-retentive layer built in, or an inner tube extruded from butyl rubber may be used. Butyl rubber, although a very “dead” rubber, has outstanding resistance to passage of air. The modern automobile, in addition to tires, uses rubber in window channels, weather-strip, wiper blades, motor mounts, cushions, and sound deadening, to the extent of about 115 kg of rubber per vehicle.

Radial tires require a different method of assembly from the traditional bias cord tires as shown in Fig. 36.8. Belts of rayon, polyester, fiberglass, and steel are all being used.

## **LATEX COMPOUNDS**

Concentrated latices permit the use of rubber as a liquid which may be spread, painted, dipped, or whipped into a foam. Suspensions of compounding ingredients provide cure, but reinforcement is not nearly as effective. The use of latex is increasing, although the foam mattress, pillow, and upholstering trades have veered toward polyurethane and polyether rubbers for their supply.

## **RECLAIMED RUBBER**

Reclaim is a useful compounding ingredient produced from scrap rubber goods.<sup>19</sup> Articles are ground finely, and rubber, fabric, metals, etc., separated by combinations of chemical, mechanical, and solution methods. Reclaimed rubber is partially depolymerized and contains a high percentage of carbon black (or other pigment), ash, and solvent oils. It imparts some desirable processing character to rubber compounds but is usually used as a cheap scrap material for very cheap products. Worldwide, only about 10 percent of new rubbers are reclaimed.

The recent increased cost of energy has spurred interest in using tire waste as fuel. The burning of 1 kg of rubber produces 7.17 MJ compared with 5.26 MJ for coal. Chunks of old tires have also been mixed with asphalt to produce an asphalt-road aggregate which has many advantages over ordinary asphalt. This Swedish process, called Plus-Ride in the United States, produces roadways that last more than four times longer, have increased traction and lower noise and glare than regular asphalt roadways.

## **RUBBER DERIVATIVES**

Rubber, particularly natural rubber, has been used as a raw material for chemical reactions to yield various derivatives of altered nature. Plastic technology is displacing these rubber-

<sup>19</sup>Paul, Reclaiming Rubber, *CHEMTECH* 9 (2) 104 (1979); *Chem. Eng. News* 58 (19) 22 (1980); *Chem. Week* 128 (23) 18 (1981).

based chemicals, for rubber is obviously an expensive raw material. Halides react with rubber, adding at the double bonds, to form chlorinated rubbers (or bromide and iodide may be used) which are useful as paint ingredients and are resistant to chemical attack. The action of hydrogen chloride on a benzene solution of rubber produces rubber hydrochloride, decidedly different from rubber in many ways. A tough, transparent plastic, it forms films used for packaging. Rubber hydrochloride is resistant to chemical attack, forms excellent thin films, and is colorless, odorless, and tasteless. PVC, polyethylene, polypropylene, and newer plastics are limiting the use of expensive rubber hydrochloride. Rubber and resin blends are widely used, the rubber adding its peculiar properties of impact resistance, extensibility, and resilience.

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# PART 2



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# Chapter 1

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## **Energy, Fuels, Air Conditioning, and Refrigeration**

As a rule, a chemical engineer is not enough of a specialist to be capable of adequately designing plants for power production, refrigeration, or air conditioning. Since the chemical process industries consume more than one-third of the energy used by *all* the manufacturing industries, chemical engineers should be familiar with the broad technical aspects of energy production and use. They should also be prepared to work with power, refrigeration, and air conditioning engineers for the proper coordination of the production of these essential tools and their use in chemical processes in order to obtain the cheapest manufacturing cost. Frequently, the cost of energy, particularly if it is to be used electrochemically, is the deciding factor in choosing the location of a factory. Process industries under the direction of chemical engineers are in most instances large consumers of steam for evaporation, heating, and drying. Consequently, these industries need large quantities of low-pressure steam. Occasionally, however, certain exothermic reactions, such as the contact sulfuric acid process, can be employed to generate steam and electricity for external use. If a steam power plant is to be used only for electrical power generation, the turbines are run condensing; if, on the other hand, both electricity and low-pressure steam for heating are needed, it is economical to lead the high-pressure steam directly from the boiler through noncondensing turbines. This uses the turbines as power-producing pressure reducers and yields exhaust steam from the prime movers to supply low-pressure steam for drying, evaporation, or other heat-users throughout the plant.

### **ENERGY**

The increased worldwide consumption of energy has led to a search for new energy sources for the future, and this has become one of the foremost objectives of science, engineering, and government.

It is estimated that in 1850 coal, oil, and gas supplied 5 percent of the world's energy, and the muscles of humans and animals, 94 percent. Today, coal, oil, gas, and nuclear sources account for approximately 94 percent, water power about 1 percent, and the muscles of humans and animals the remaining 5 percent. Of the total amount of coal, oil, and gas that has been burned for the benefit of humans up to this time, less than 10 percent was burned